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Toward bifunctional doped MnO_2 oxygen electrocatalyst

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Processes of oxygen electroevolution (OEER) and electroreduction (OERR) is supposed to be important constituent part of water splitting technologies, sustainable energy generation such as fuel cells, metal-air batteries or regenerative fuel cells. Despite the excellent prospectives and theoretical electrical performance of them new findings and developments are still necessary. The example where improvements are crucial to make it practically available is the Lithium-air battery (LAB) technology [1, 2, 3].

Oxides of transition metals with tailor-made properties are good candidates for LAB-applications as alternative to noble metals materials. Manganese dioxide has many advantages among other transition metals. It has high ORR activity, it is one of the best H_2O_2 decomposition catalysts, it found practical application in Zn-air batteries for decades in addition to low cost and environmental friendliness [4].

On the other hand, electrocatalytic activity in both reduction and oxidation processes of a single compound is rare. Therefore, special bifunctional catalysts have been developed for LAB technologies. The bifunctionality is well-known in chemistry. For instance, many bifunctional catalysts in organic chemistry possess either Lewis or Brønsted basic functionality. Compared to single functional group catalysts, the cooperative effect of the two complementary functional groups can lead to new reactivity and stereocontrol in reactions that were previously challenging or

unprecedented [5].

There are generally two strategies to improve the activity (or reaction rate) of an electrocatalyst system: (i) increasing the number of active sites on a given electrode (e.g. through increased loading or improved catalyst structuring to expose more active sites per gram), or (ii) increasing the intrinsic activity of each active site [6]. At the same time, there are physical limits to how much catalyst material can be loaded onto an electrode without affecting other important processes such as charge and mass transport. The difference between a good catalyst and a poor catalyst can be more than 10 orders of magnitude apart, whereas the difference between a high loading and a low loading catalyst might only be 1 to 3 orders of magnitude [7].

The electrolytic doping procedure has been developed in our research group [8, 9]. As shown recently, phase and chemical composition of electrocrystallisation product is dependent on dopant additive nature and concentration in an electrolyte. The electrochemical properties in this case are subjected to changes that otherwise are difficult to achieve. Enhanced electrocatalytic activity of Fe-doped MnO_2 in phenol and VOC degradation was shown in [9], the peculiarities of electrocatalytic activity of doped MnO_2 samples in oxygen electroreduction are also under consideration [10].

Manganese(IV) oxides are among the most effective non-precious (electro)catalysts of both oxidation and reduction processes, nevertheless there is a necessity to develop bifunctional catalysts that activate simultaneously oxidation and reduction. The phase composition and structure defects have profound influence on this material activity. The purpose of this work was to study influence of induced by dopant ions changes on ability of manganese(IV) oxides to be oxygen electrocatalyst.

1. Experimental

Manganese(IV) oxide samples were electrodeposited galvanostatically (i = 10 A/dm^2) at the platinum plate anode and the vitreous carbon plate as an auxiliary electrode. The pristine fluorine-containing electrolyte consisted of 0.1 M HF + 0.7 M $MnSO_4$ and the dopant additives in the electrolyte were sulfates of the following concentration: 1.5 M NH_4^+, 0.01 M Fe^{2+}, 0.01 M Cr^{3+}, 0.01 M Co^{2+}. Some samples

were prepared using trinary electrolytes by ions of metals. They contained besides manganese sulfate and hydrofluoric acid HF additives of cobalt sulfate and lithium hydroxide. The dopant ions were introduced by the addition of 0.03—1 M of CoSO4 and 0.1—4 M LiOH. The concentration of manganese ions was also varied in the range 0.1—0.7 M. XRD study was performed on a DRON 4 instrument (Mo and Cu$K\alpha$-radiation).

The cyclic voltammetry (CVA) experiment was carried out in a standard three electrode cell and 0.3 M LiOH electrolyte saturated with O_2 on IPC-PRO potentiostat – galvanostat at the potential scan rate to within 0.001–0.5 V/s. Carbon paste electrode (CPE) was assembled to study manganese dioxide samples electrocatalytic activity in ORR. CPE was a thoroughly grounded mixture of doped manganese oxide: graphite in the ratio 70:30 and polytetrafluoroethylene (PTFE) emulsion loaded into PTFE-tube.

2. Results and discussion

The XRD phase analysis showed the following main phase components depending on dopants added (Table 1). These results are in agreement with thermodynamics of hollandite phase since foreign ions like NH_4^+ in structure channels decrease its free energy significantly [4] as a result of influence of entropic factor. The template doping effects of M^+-ions on hollandite or α-MnO_2 stabilisation allow realization of electrocatalyst with structure tunnel size available for small molecules of water and organics. Ramsdellite or γ-MnO_2 is crystallised with additives of transition metals (Fe^{2+}, Co^{2+}) and at the presence of Cu^{2+} both effects take place. The low concentrations of Cu^{2+} additive (0.001-0.002 M) stabilize hollandite structure but the increase its content by the order of magnitude changes hollandite to semiamorphous ramsdellite phase and β-MnO_2. The layered birnessite structure is formed at the presence of Cr^{3+} additives.

Table 1. Chemical and phase composition of doped manganese dioxide samples obtained by anode electrodeposition at the presence of ionic additives from fluorinecontaining electrolytes.

Samples	1	2	3	4
Origin/dopant	NH_4^+	Cr^{3+}	Fe^{2+}	Co^{2+}
Dopant ion concentration in electrolyte, mol/L	1.5	0.001	0.01	0.01
Mn (total), mas. %	59.7	55.2	44.2	45.2
Dopant ion content in samples, mas. %	-	3.9	0.26	0.012
Phase components	α+γ	δ+α	γ+β	Γ

As shown by XRD-data, significant additional broadening of (110) ramsdellite main XRD-pattern peak is observed at the presence of 0.001-0.01M Co^{2+}. The same tendency is less distinctive for Fe^{2+} due to its reducing activity in an electrolyte. These features are the results of the heterovalent substitution of transition metals that occupy Mn position in crystal lattice. Crystal chemistry gives the evidences in favour of this behavior of dopant additives. Isostructural to ramsdellite structure compounds exist (*Pnma* with orthorhombic symmetry of heterogenite CoOOH — groutite β-MnOOH — ramsdellite γ-MnO_2 — goethite, α-FeOOH). Therefore, the simultaneous presence of these metals in an electrolyte gives prerequisites of solid solutions formation. Conditions of their preparation require further investigations. The results of XRD study of heavy doped by Co-samples in comparison with heterogenite XRD pattern are shown in Fig. 1. To summate mentioned above facts, the prospective of active site concentration increase is realized in case of Mn^{4+} sites heterovalent substitution by Fe^{2+}, Co^{2+} and etc.

CVAs of doped MnO_2 CPE in 0.30 M LiOH solution saturated with oxygen were studied at V=20 $mV \cdot s^{-1}$. Peaks of ORR become visible in mA range of currents in our CVA experiments after electrolyte saturation by oxygen or prolonged anode polarisation at potentials higher than 1 V (vs Ag/AgCl) at oxygen evolution. The

weak two steps of ORR can be seen in the range of potentials -0.2 and 0.7 V and are the charge transfer controlled with the Tafel slopes *b* that are in agreement with 60 and 120 mV of ORR detected on Pt electrode correspondingly [11]. OER peaks are observed at the reverse direction of CVA scan after about 1.0 V.

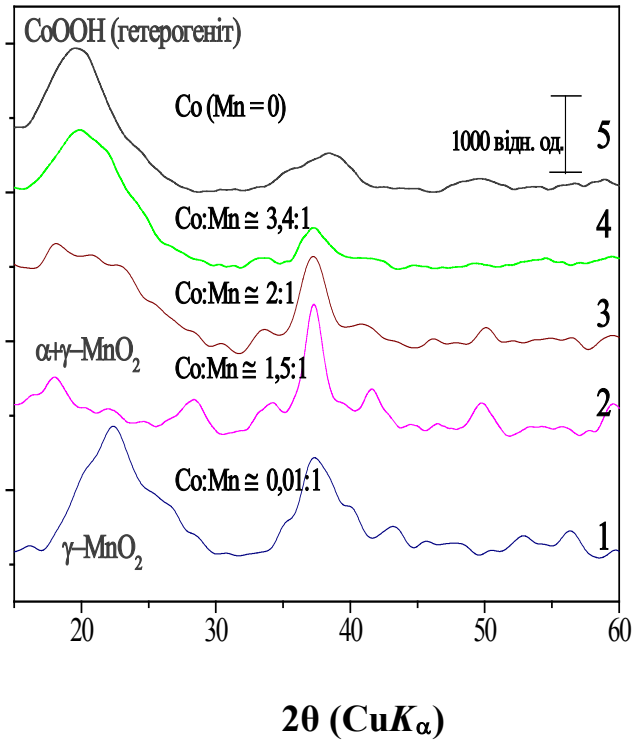

Fig. 1. XRD patterns of doped by Co and Li samples with different ration Co:Mn in an electrolyte in comparison with Co containing electrolyte

Analysis of ORR activity of investigated samples is shown in Table 2. Fe^{2+}, and Co^{2+} doped samples display similar behaviour with two weak peaks of ORR currents. These samples have two well-defined $2e^-$ steps of ORR with maximal current unlike Samples 1-3. ΔE ($E_{OER} - E_{ORR}$) is close to 1.0 V which is in agreement with published data [12]. The anode current of OER makes up 56 mA/cm^2 for sample 1 which is evaluated from steady state polarisation curve and it is by about 40 times larger than ORR currents on this sample.

The electrolytic doping procedure improves the prospective of practical application of electrodeposited manganese(IV) oxides as electrocatalyst. The high activity of Fe^{2+}-doped MnO_2 indicates the positive role of Fe^{3+}/Fe^{2+} redox pairs as active sites of surface states. Doped by Co^{2+} samples display high activity and some unique features in ORR(OER) also. It is proposed that combination of Co^{2+} and Fe^{2+} additives could be prospective as a bifunctional catalyst for LAB cathode application.

Table 2. ORR electrochemical parameters of samples 1-4 (V = 0.02 V/s)

Sample	1	2	3	4
	NH_4^+	Cr^{3+}	Fe^{2+}	Co^{2+}
ORR E_1, V	-	-	0.547	0.544
I_1, mA/cm^2	-	-	1.18	1.38
ORR E_2, V	-0.028	-0.111	0.023	-0.015
I_2, mA/cm^2	1.24	0.56	0.29	0.33

3. Conclusion

The electrolytic doping procedure developed in our research group obeys both strategy principles in improving electrocatalyst efficiency, i.e. increasing the number of active sites and intrinsic activity. The directed changes of phase composition increase intrinsic activity of surface sites comparing with conventional electrodeposition methods. The prospective of active site concentration increase is realized in case of heterovalent substitution by Fe^{2+}, Co^{2+} and etc.

The electrolytic doping procedure expands practical application of electrochemical manganese dioxide due to the control of chemical and phase compositions. The ionic dopant additives of NH_4^+, Fe^{2+}, Co^{2+} have different mechanisms of their influence upon electrocrystallisation process. The electrolytic doping procedure improves the prospective of practical application of electrodeposited manganese(IV) oxides as electrocatalyst. Both doped by Co^{2+} and Fe^{2+} ions samples display the best activity and some unique features in ORR(OER). It is proposed that combination of Co^{2+} and Fe^{2+} additives could be prospective as a bifunctional catalyst for LAB cathode application. The high activity of Fe^{2+}-doped MnO_2 indicates the positive role of Fe^{3+}/Fe^{2+} redox pairs as active sites of surface states.

References

[1] Z. Zhang, J. Liu, J.Gu, L. Su, L. Cheng, *Energy Environ. Sci*., 2014, 7, 2535.

[2] C. Fangyi, C. Jun, *Chem. Soc. Rev*., 2012, 41, 2172.

[3] J.W.D. Ng, Y. Gorlin, T. Hatsukade, F.T. Jaramillo, *Adv. Energy Mater.,* 2013, *3,* 1545.

[4] K.A. Stoerzinger, M. Risch, B. Han, Y. Shao-Horn, *ACS Catal.,* 2015, *5* (10), 6021–6031.

[5] Dixon, D. J. *Beilstein J. Org. Chem.* 2016, *12,* 1079–1080.

[6] Seh, Z. W., Kibsgaard, J., Dickens, C. F., Chorkendorff, I. B., Nørskov, J. K., & Jaramillo, T. F. (2017). *Science*, *355*(6321), eaad4998

[7] J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont, T. F. Jaramillo, Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials. ACS Catal. (2014) 4, 3957-3971.

[8] Sokolsky, G. V., Ivanov, S. V., Boldyrev, E. I., Ivanova, N. D., & Lobunets, T. F. *Solid State Phenomena* (2015) 230, 85-92.

[9] Sokol'skii, G. V., Ivanova, S. V., Ivanova, N. D., Boldyrev, E. I., Lobunets, T. F., & Tomila, T. V. (2012). *Journal of Water Chemistry and Technology*, *34*(5), 227-233.

[10] Sokolsky, G., Zudina, L., Boldyrev, E., Miroshnikov, O., Gauk, N., & Kiporenko, O. (2018). *Acta Physica Polonica A*, *133*(4), 1097-1102.

[11] C.Song, and J.Zhang, Eds J.Zhang, in: PEM Fuel Cell Electrocatalysts and Catalyst Layers: Fundamentals and Applications, Springer, London 2008, p. 89.

[12] Chung-Hao Kuo, I.M.Mosa, S.Thanneeru, V.Sharma, Lichun Zhang, et al. Chem. Commun. 51,5951 (2015).